

WHAT IS CLAIMED IS:

1. A method for preparing an anodized electrode comprising the sequential steps of:
 - (1) providing a substrate;
 - (2) coating the surface of the substrate by vacuum deposition thereon of a porous coating comprising at least one substance selected from valve metals, valve metal oxides and mixtures thereof;
 - (3) increasing the effective surface area of the porous coating; and
 - (4) producing electrolytically at least one anodized valve oxide layer overlaying the surface of the porous coating.
2. A method according to claim 1, wherein the effective surface area increase of the porous coating is implemented by at least one of the following:

increasing the total pore volume of the porous coating;
increasing the average pore width in the porous coating.
3. A method according to claim 1, which is further characterized by at least one of the following features:
 - (a) the substrate is an electrically conductive substrate;
 - (b) the porous coating comprises at least one member selected from aluminum, aluminum oxide and mixtures thereof;
 - (c) the at least one electrolytically produced layer comprises aluminum oxide;
 - (d) the effective surface area increase has been implemented by at least one procedure selected from:

electrochemical etching; and
oxidizing the surface of the porous layer followed by removal of thus formed oxide;
 - (e) prior to deposition of the porous coating, the surface of the substrate has been subjected to a roughening procedure selected from mechanical, chemical and electrochemical procedures;
 - (f) said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr.;

(g) said vacuum deposition is carried out in an inert gas atmosphere in presence of a minor amount of oxygen;

(h) following said step (4), the product is thoroughly rinsed with a liquid selected from distilled and de-ionized water, and then dried.

4. A method according to claim 3, which is further characterized by at least one of the following features:

(A) the electrically conductive substrate is a metallic foil substrate;

(B) said step (3) is implemented by electrolytic anodization and simultaneously or subsequently removing electrolytically formed valve metal oxide.

5. A method according to claim 4, wherein said step (4) is carried out by forming at least two anodized layers, and the product is subjected to annealing prior to the last of said at least two anodization steps.

6. A method according to claim 5, wherein the product is thoroughly rinsed with a liquid selected from distilled and de-ionized water, prior to said annealing.

7. A method according to claim 4, wherein the substrate is a metallic foil substrate; in said step (2) the at least one valve metal comprises aluminum; in said step (3) said increasing is implemented by oxidizing the surface of the initial layer by anodization in presence of an electrolyte which comprises a saturated dicarboxylic acid salt selected from the ammonium and alkali metal salts, and removing thus-formed valve metal oxide(s) by use of a halogen-free chemical etchant *in situ* or in a discrete subsequent sub-step; and in said step (4) the at least one layer comprises aluminum oxide.

8. A method according to claim 7, wherein said step (4) is carried out by forming at least two anodized layers, and the product is subjected to annealing prior to the last of said at least two anodization steps.

9. A method according to claim 7, wherein at least one of the following features applies:

said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr. in presence of a minor amount of oxygen;

the electrolyte comprises a salt selected from the ammonium and alkali metal adipates;

the chemical etchant is selected from chromic, oxalic and phosphoric acid, and mixtures thereof.

10. A method according to claim 8, wherein at least one of the following features applies:

said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr. in presence of a minor amount of oxygen;

the electrolyte comprises a salt selected from the ammonium and alkali metal adipates;

the chemical etchant is selected from chromic, oxalic and phosphoric acid, and mixtures thereof.

11. A method according to claim 4, wherein the substrate is a metallic foil substrate; in said step (2) the at least one valve metal consists essentially of aluminum and the vapor deposition is carried out in presence of a minor amount of oxygen such that the porous layer consists essentially of aluminum metal and aluminum oxide; in said step (3) said increasing is implemented by oxidizing the surface of the initial layer by anodization in presence of an electrolyte which comprises a saturated dicarboxylic acid salt selected from the ammonium and alkali metal salts, and removing thus-formed valve metal oxide(s) by use of a halogen-free chemical etchant *in situ* or in a discrete subsequent sub-step; and in said step (4) the at least one layer comprises aluminum oxide.

12. A method according to claim 11, wherein said step (4) is carried out by forming at least two anodized layers, and the product is subjected to annealing prior to the last of said at least two anodization steps.

13. A method according to claim 11, wherein at least one of the following features applies:

said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr.;

said vacuum deposition conditions are such that the porous layer prior to step (3) consists essentially of at least 40% aluminum metal, balance aluminum oxide;

the electrolyte comprises a salt selected from the ammonium and alkali metal adipates;

the chemical etchant is selected from chromic, oxalic and phosphoric acid, and mixtures thereof.

14. A method according to claim 11, wherein at least one of the following features applies:

said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr.;

said vacuum deposition conditions are such that the porous layer prior to step (3) consists essentially of 50-85% aluminum metal, balance aluminum oxide;

the electrolyte comprises a salt selected from the ammonium and alkali metal adipates;

the chemical etchant is selected from chromic, oxalic and phosphoric acid, and mixtures thereof.

15. A method for preparing an anodized electrode which includes pores having a branched morphology, comprising the sequential steps of:

(1) providing a metallic foil substrate;

(2) coating the surface of the substrate by vacuum deposition thereon of aluminum vapor in presence of a minor amount of oxygen such that a porous layer, consisting essentially of an aluminum metal component and an aluminum oxide component, is deposited on the substrate;

(3) increasing the effective surface area of the porous coating by electrolytic anodization in presence of an electrolyte which comprises a saturated dicarboxylic acid salt selected from the ammonium and alkali metal salts, and removing thus-formed valve metal oxide(s), as well as at least part of the aluminum oxide component, by use of a halogen-free chemical etchant *in situ* or in a discrete subsequent sub-step; and

(4) producing electrolytically at least one anodized aluminum oxide layer overlaying the surface of the porous coating.

16. A method according to claim 15, wherein at least one of the following features applies:

said vacuum deposition is carried out in an inert gas atmosphere at a pressure of between about 10^{-3} Torr. and about 10^{-2} Torr.;

said vacuum deposition conditions are such that the porous layer prior to step (3) consists essentially of at least 40% aluminum metal, balance aluminum oxide;

the electrolyte comprises a salt selected from the ammonium and alkali metal adipates;

the chemical etchant is selected from chromic, oxalic and phosphoric acid, and mixtures thereof.

17. A method according to claim 16, wherein said step (4) is carried out by forming at least two anodized layers, and the product is subjected to annealing prior to the last of said at least two anodization steps.

18. An anodized electrode comprising:

a substrate;

a porous coating on the surface of said substrate produced by vacuum deposition thereon, said porous coating comprising at least one substance selected from valve metals, valve metal oxides and mixtures thereof; and

at least one electrolytically produced anodized layer selected from valve metal oxides and mixtures thereof;

wherein in said porous coating, the effective surface area has been increased prior to deposition of said at least one anodized layer.

19. An anodized electrode according to claim 18, which is further characterized by at least one of the following features:

(a) said substrate is an electrically conductive substrate;

- (b) said porous coating comprises at least one member selected from aluminum, aluminum oxide and mixtures thereof;
- (c) at least one anodized layer comprises aluminum oxide;
- (d) said effective surface area increase has been implemented by oxidizing the surface of said porous layer and removing thus formed oxide;
- (e) prior to deposition of said porous coating, the surface of said substrate has been subjected to a roughening procedure selected from mechanical, chemical and electrochemical procedures.

20. An anodized electrode according to claim 19, wherein said porous coating consists essentially of aluminum and aluminum oxide and said at least one anodized layer consists essentially of aluminum oxide.

21. An anodized electrode according to claim 20, wherein prior to effective surface area increase and anodization, said porous coating consists essentially of 50-85% aluminum metal, balance aluminum oxide.

22. An anodized electrode according to claim 18, wherein said effective surface area increase had been implemented by at least one of the following:
increasing the total pore volume of said porous coating;
increasing the average pore width in said porous coating.

23. An anodized electrode which comprises non-cylindrical pores having a branched morphology.

24. An anodized electrode according to claim 23, wherein at least some of said pores are generally configured as inverted cones.